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CALCULATION OF THE ENERGETICS AND COLLISION DYNAMICS OF ELECTRO--ETC(U)
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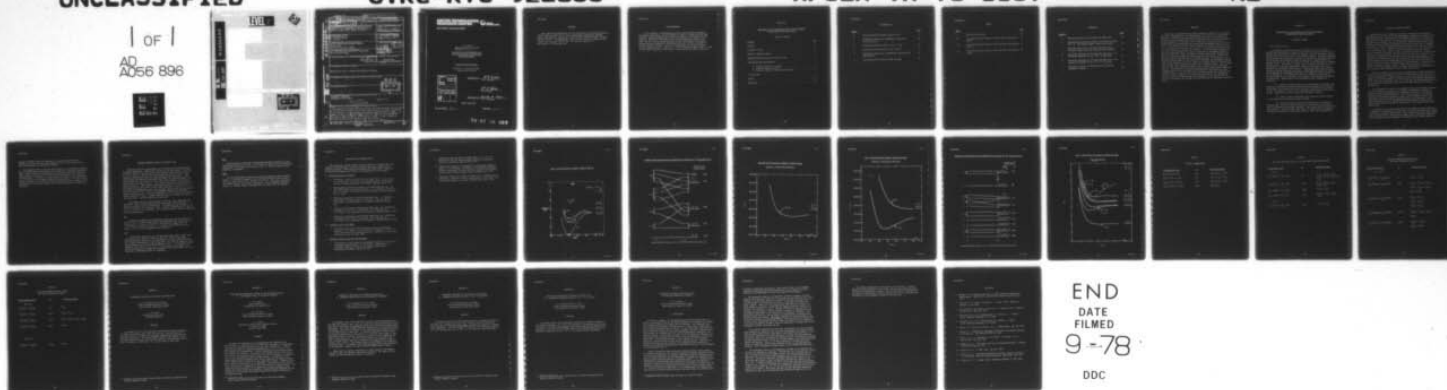
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The research performed under this contract was directed toward the calculation of the electronic structure of selected chemical systems in order to determine their potential as laser systems. The systems studied included the symmetry of Hg_2^+ , the $A^2\Sigma_u^+$ and $B^2\Sigma_u^+$ states for Hg_2^+ , all low-lying 2Σ and 2Π states of $MgNa$ and the 2Σ and 2Π states of $HgTl$. A list is given of the publication and talks resulting from this program. $2 \sigma_g(+), sub u$ $2 \sigma_g(+), sub g$		

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Calculation of the Energetics and
Collision Dynamics of Electronic
Transition Lasers

Interim Scientific Report

Contract No. F49620-77-C-0064
Project-Task 2303/B1

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FOREWORD

This report was prepared for the Air Force Office of Scientific Research, United States Air Force by the United Technologies Corporation, Research Center, East Hartford, Connecticut, under Contract F49620-77-C-0064, Project-Task No. 2303/B1. The performance period for the technical program was from 1 April 1977 through 31 March 1978. The project monitor was Major Robert A. Osteryoung, USAF.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the advise and assistance rendered by the author's associates. We are indebted to Judith B. Addison for her help both with computer programming and with the analysis of the results of this research. Her efforts have been of real value during the course of this work. We also wish to acknowledge many fruitful discussions with research associates and the beneficial collaboration with Dr. Gerald A. Peterson on several research problems. Finally, we acknowledge the continued support and encouragement given by Lt Col. John T. Viola of AFOSR and Major David S. Olson of AFWL whose confidence in the value of this research has been of real help.

R78-922853

Calculation of the Energetics and Collision Dynamics
of Electronic Transition Lasers

TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
ABSTRACT	1
STATEMENT OF WORK	2
REVIEW OF TECHNICAL EFFORT	3
RESEARCH PROGRESS DURING THE CONTRACT YEAR	5
PUBLICATIONS AND PRESENTATIONS	7
A. Technical Reports in Journals	7
B. Technical Reports in Books	7
C. Technical Paper and Lecture Presentations	9
ILLUSTRATIONS	9
TABLES	15
APPENDICES	19

ILLUSTRATIONS

<u>Figure</u>		<u>Page</u>
1	Low-Lying Potential Energy Curves for SiF	9
2	Correlation Diagram for Intermediate Coupling of the Hg_2 Molecule	10
3	Ground State Potential Energy Curve for Hg_2	11
4	Low-Lying Potential Energy Curves for Hg_2^+	12
5	Correlation Diagram for Intermediate Coupling of the HgTl Molecule	13
6	Low-Lying Potential Energy Curves for MgNa	14

TABLES

<u>Table</u>		<u>Page</u>
I	SiF/SiF ₂ Correlations	15
II	Low-Lying Molecular States of SiF and Their Dissociation Limits	16
III	Low-Lying Molecular States of Hg ₂ ⁺ and Their Dissociation Limits	17
IV	Low-Lying Molecular States of MgNa and Their Dissociation Limits	18

APPENDICES

<u>Appendix</u>		<u>Page</u>
A	Electronic Structure of the Noble Gas Dimer Ions	19
B	Configuration Interaction Studies of the HeH^+ Molecular Ion. IV. The Triplet Sigma, Pi and Delta States	20
C	Electronic Structure of the Noble Gas Dimer Ions. I. Potential Energy Curves and Spectroscopic Constants	21
D	Electronic Structure of the Noble Gas Dimer Ions. II. Absorption Spectrum for the $A \ ^2\Sigma_u^+ \rightarrow D \ ^2\Sigma_g^+$ System	22
E	Electronic Structure of the Noble Gas Dimer Ions. III. Absorption Spectrum for the $A \ ^2\Sigma_u^+ \rightarrow B \ ^2\Pi_g$ System	23
F	Electronic Structure of Excited States of Selected Atmospheric Systems	24

ABSTRACT

Knowledge of the partition of energy between the products of a chemical reaction is fundamental to the understanding of the dynamics of collisional reactions. Atom-atom and atom-molecule reactions that yield vibrationally excited diatomic molecules are of particular scientific and military interest. An understanding of the dynamics of the simplest of these reactions is a prerequisite for understanding more complicated rearrangement gas phase reactions. A knowledge of at least limited regions of potential energy surfaces is of importance in analyzing the vibrational and rotational relaxation rates and can be utilized in a predictive fashion. In the low energy regime there are little data available on collision processes and experimental measurements are difficult. Thus, a program to develop theoretical techniques and construct computer programs for calculating potential energy surfaces and kinetic cross sections for simple collision processes is appropriate. The potential energy surfaces will include both atom-atom and atom-diatom systems with special emphasis on molecular reactions yielding electronically excited products which have potential as visible or UV chemical lasers. These systems shall include metal oxides and halides, metal excimers and the noble gas-halides. This research will develop techniques and computational schemes for a priori prediction of the kinetics and the product distribution of atom-diatom reactions. This will involve (1) improved calculation techniques for potential energy surfaces for the reactants and products, (2) quantum and classical mechanical calculations of the dynamics of the reaction and (3) detailed calculations for systems with high potential as electronic transition lasers.

R78-922853

Calculation of the Energetics and Collision Dynamics
of Electronic Transition Lasers

STATEMENT OF WORK

The contractor shall:

a. Perform a theoretical research investigation of the electronic structure and energetics of excimer systems and on chemical reactions in such systems which would yield a sufficient density of excited electronic species capable of lasing in the visible or UV spectrum regions. Calculate electronic wave-functions and energies as a function of internuclear separation followed by calculations of electronic transition moments for systems selected as typical of this class, and which appear to offer a high potential as candidate excimer lasers. In addition, research shall be carried out related to the development of practical computational techniques for prediction of the kinetics and the product distribution of chemical reactions involving electronically excited reactants or products. Experimental data will be iteratively examined and integrated with the results generated from this theoretical investigation. The computations shall be carried out using density functional and ab initio methods, using computer codes developed or modified at this Center. Specifically, this investigation shall comprise the following:

(1) Conduct research related to the development of practical computational techniques for defining potential energy surfaces for reactants and products with possible electronic excitation and illustrate the utility of such techniques by a study of the long-range interactions in the $\text{Si} + \text{F}_2$ system. This portion of the research has the highest priority.

(2) Survey existing experimental and theoretical data available to the Contractor pertaining to excimer systems.

(3) Perform quantum mechanical calculations of the electronic wavefunctions, electronic transition moments, and radiative lifetimes for three (3) diatomic metal excimer systems. These systems shall be chosen from the following: Hg_2 , Cd_2 , CdHg , TlHg , TlCd . If other chemical systems are subsequently identified as potential candidates these can be substituted.

REVIEW OF TECHNICAL EFFORT

Calculations of the dynamics of molecular collisions are ordinarily carried out with the aid of the Born-Oppenheimer separation of the electronic and nuclear motion. One proceeds by calculating the electronic energy as a function of the positions of the nuclei, which are assumed to be stationary. This electronic energy, plus the electrostatic repulsion between the nuclei, defines a potential energy hypersurface on which the nuclei may be regarded as moving. A potential energy hypersurface defined in this way is referred to as adiabatic, and is appropriate for describing the nuclear motion in the limit of low velocity. There are many collisions for which an adiabatic potential energy hypersurface provides an adequate description. However, most reactive collisions and many collisions which do not lead to reaction are inadequately described by an adiabatic potential energy hypersurface. These collisions are characterized by velocities of nuclear motion sufficient to affect adversely the Born-Oppenheimer separation, with the result that the overall wavefunction must be described as a superposition of terms involving different electronic energy states. Under these conditions, it will be useful to consider adiabatic potential energy hypersurfaces corresponding to all electronic states relevant to the overall wavefunction.

When the different potential energy hypersurfaces are well separated in energy, the nuclear motion can ordinarily be described in terms of motion on a single hypersurface. However, when two or more hypersurfaces are close in energy, they can be expected to mix appreciably in the overall wavefunction, and it will then be necessary not only to calculate the hypersurfaces but also to calculate the quantities needed to discuss their mixing in the overall wavefunction.

The calculation of a point on a potential energy hypersurface is equivalent to calculating the energy of a diatomic or polyatomic system for a specified nuclear configuration, and therefore will present considerable practical computational difficulty. For certain problems or nuclear configurations, the maximum possible accuracy will be needed and under these conditions relatively elaborate ab initio methods are indicated. Under other conditions, it may be possible to use less elaborate and more rapid computational methods, and density functional or other approaches may then prove useful.

A knowledge of at least limited regions of potential energy surfaces is of importance in analyzing the electronic, vibrational and rotational relaxation rates in chemical laser systems. These relative relaxation rates govern both the feasibility of lasing and the power that is potentially available. Such relaxation rates are governed by long-range forces between atomic and

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molecular fragments and thus knowledge of the dissociation behavior represented by the potential energy surfaces for the laser system can be used in calculations of the kinetic behavior.

Our reserach effort to date has been devoted to the theoretical development of computational techniques for the prediction of potential energy surfaces, and to studies of the energetics of prototype electronic transition laser systems, the prediction of the radiative lifetimes of electronically excited species, and studies of photon energy loss paths such as photoabsorption or ionization of the upper excited electronic states. The goal of this research program is to develop a technical information base in support of the development of a practical chemical laser system operating on an electronic transition.

RESEARCH PROGRESS DURING THE CONTRACT YEAR

Electronic structure calculations were performed for the Si+F₂ system at various geometries. Studies were carried out for the ground X ¹A₁ state, the first excited A ¹B₁ state and for the separated atom-molecule states of Si (³P) + F₂(¹Σ_g⁺). The SiF/SiF₂ correlations are shown in Table I. Our calculated excitation energy is in good agreement with experiment. These calculations also indicate a maximum in the lowest ¹A₁ potential energy surface relative to Si+F₂ similar to that found in the diatomic molecule SiF. These results are shown in Fig. 1. The corresponding atomic correlations are given in Table II. The origin of the maximum in the A ²Σ⁺ state of SiF is an avoided crossing with the ²Σ⁺ ionic state connecting to Si⁺ (²P) + F⁻ (¹S). The origin of the maximum in SiF₂ is an avoided crossing with the ¹A₁ surface arising from SiF⁺(X¹Σ⁺) + F⁻(¹S). This maximum suggests that favorable branching should occur to the higher metastable a ⁴Σ⁻ state of SiF in the exothermic reaction of Si+F₂. Similar chemistry should be observed in the GeF and SnF systems. Further studies are in progress.

Calculations have also been initiated on the Hg₂, Hg₂⁺, MgNa and TlHg molecules. These studies include density functional calculations with explicit treatment of all core electrons. The symmetries O_g⁺ for Hg₂, A ²Σ_u⁺ and B ²Σ_g⁺ for Hg₂⁺, all low-lying ²Σ and ²Π states of MgNa and the ²Σ and ²Π states of HgTl have been examined. The results obtained to date are summarized for each system below.

Hg₂

A correlation diagram for intermediate coupling of the Hg₂ molecule is shown in Fig. 2. Density functional calculations have been carried out on the ground X ¹Σ_g⁺ state of the system. The potential energy curve for X ¹Σ_g⁺ of Hg₂ is presented in Fig. 3. We find a calculated dissociation energy of 0.2 eV, in good agreement with experiment.

Hg₂⁺

A correlation diagram for the low-lying molecular states of Hg₂⁺ and their dissociation limits is shown in Table III. Density functional calculations were carried out for the ground A ²Σ_u⁺ state and the excited B ²Σ_g⁺ state dissociating to the Hg ¹S_g (6s²) + Hg⁺ ²S_g(6s) asymptotic limit. These potential energy curves are presented in Fig. 4. Calculations of the radiative lifetimes for the A ²Σ_u⁺ → B ²Σ_g⁺ system is in progress. Our calculated dissociation energy for the ground A ²Σ_u⁺ state of Hg₂⁺ is 0.64 eV. There are no experimental data for comparison.

HgTl

Detailed density functional calculations have been carried out on the low-lying doublet states of HgTl. A correlation diagram for the intermediate coupling of the HgTl molecule is shown in Fig. 5. Further studies on this system are in progress.

MgNa

The low-lying doublet sigma and pi states of MgNa have been studied in detail. A correlation diagram for the low-lying molecular states of MgNa and their dissociation limits is shown in Table IV. Ab initio calculations were carried out on the $^2\Sigma$ and $^2\Pi$ symmetries. These states are presented in Fig. 6. Further studies, including the ionic state, are in progress.

PUBLICATIONS AND PRESENTATIONS

The significant research results obtained under this Contract have been prepared for publication in technical journals and books or presented at technical meetings. These papers and meetings are listed below. Abstracts of the published papers are included in the Appendices to this report.

A. Technical Reports in Journals

1. "Electronic Structure of the Noble Gas Dimer Ions". H. H. Michels, R. H. Hobbs and L. A. Wright, to be published in the International Journal of Quantum Chemistry, 1978 Sanibel Symposium Issue, 1978.
2. "Configuration Interaction Studies of the HeH^+ Molecular Ion. IV. The Triplet Sigma, Pi and Delta States." T. A. Green, H. H. Michels and J. C. Browne, to be published in the Journal of Chemical Physics, July 1, 1978.
3. "Electronic Structure of the Noble Gas Dimer Ions. I. Potential Energy Curves and Spectroscopic Constants." H. H. Michels and R. H. Hobbs, to be published in the Journal of Chemical Physics, 1978.
4. "Electronic Structure of the Noble Gas Dimer Ions. II. Absorption Spectrum for the $A \ ^2\Sigma_u^+ \rightarrow D \ ^2\Sigma_g^+$ System." H. H. Michels and R. H. Hobbs, to be published in the Journal of Chemical Physics, 1978.
5. "Electronic Structure of the Noble Gas Dimer Ions. III. Absorption Spectrum for the $A \ ^2\Sigma_u^+ \rightarrow B \ ^2\Pi_g$ System." H. H. Michels and R. H. Hobbs, to be published in the Journal of Chemical Physics, 1978.

B. Technical Articles in Books

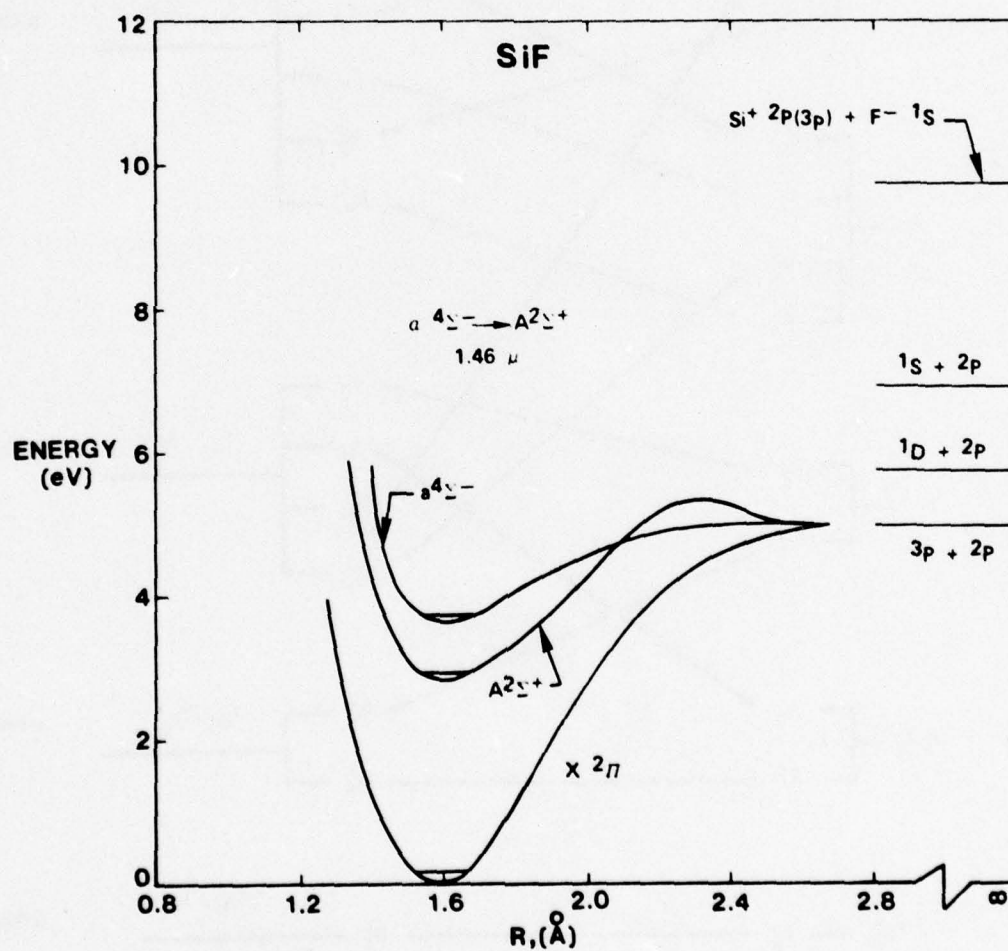
1. "Electronic Structure of Excited States of Selected Atmospheric Systems." H. H. Michels, to be published as a chapter in Volume II of the "Excited State in Chemical Physics". Edited by J. Wm. McGowan, John Wiley & Sons, New York, 1978.

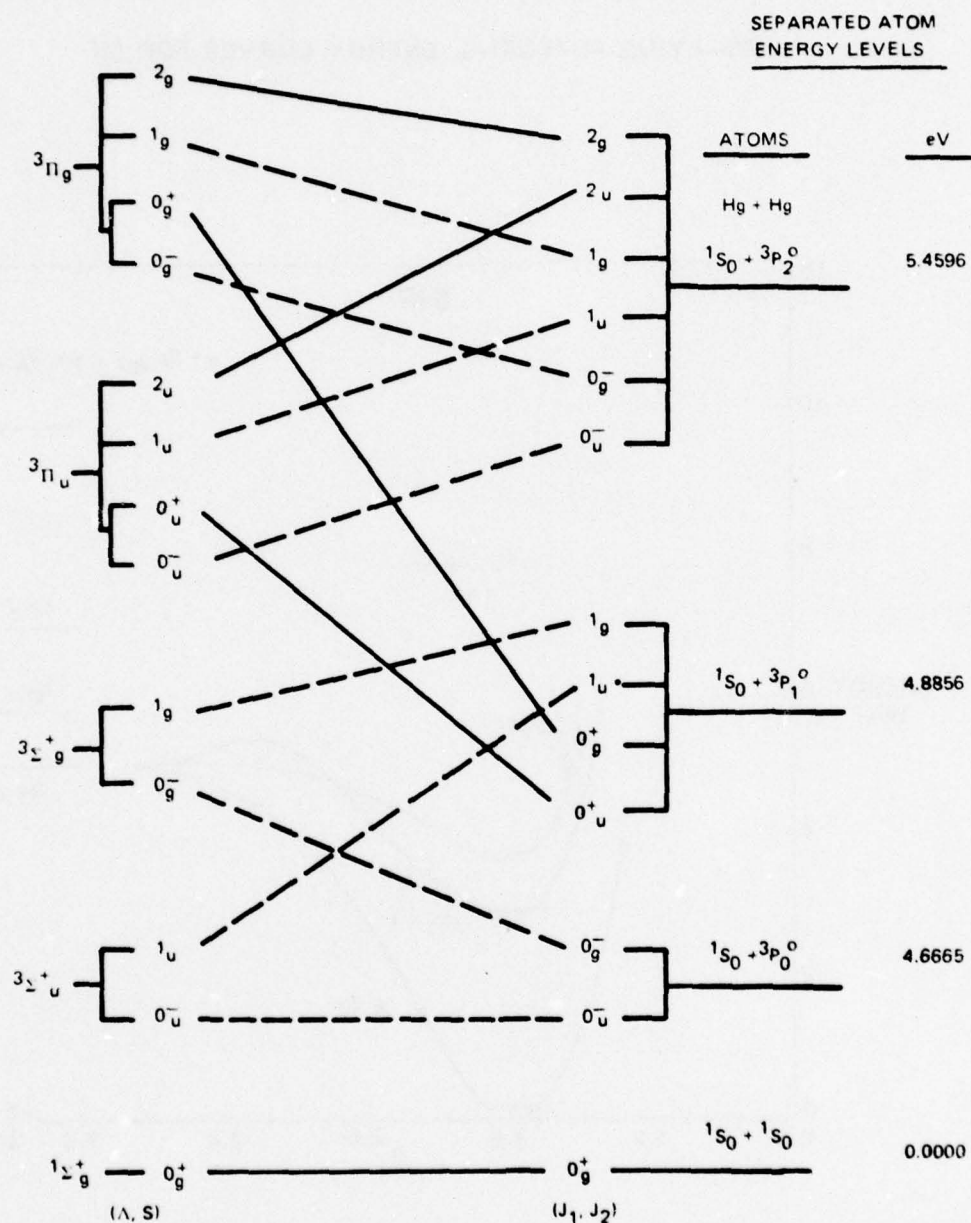
C. Technical Paper and Lecture Presentations

1. "Calculations of the Energetics and Radiative Properties of Visible/UV Chemical Laser Systems." H. H. Michels. Presented at the AFOSR/AWFL Contractors' Meeting, Kirtland Air Force Base, Albuquerque, New Mexico, May 16-20, 1977.

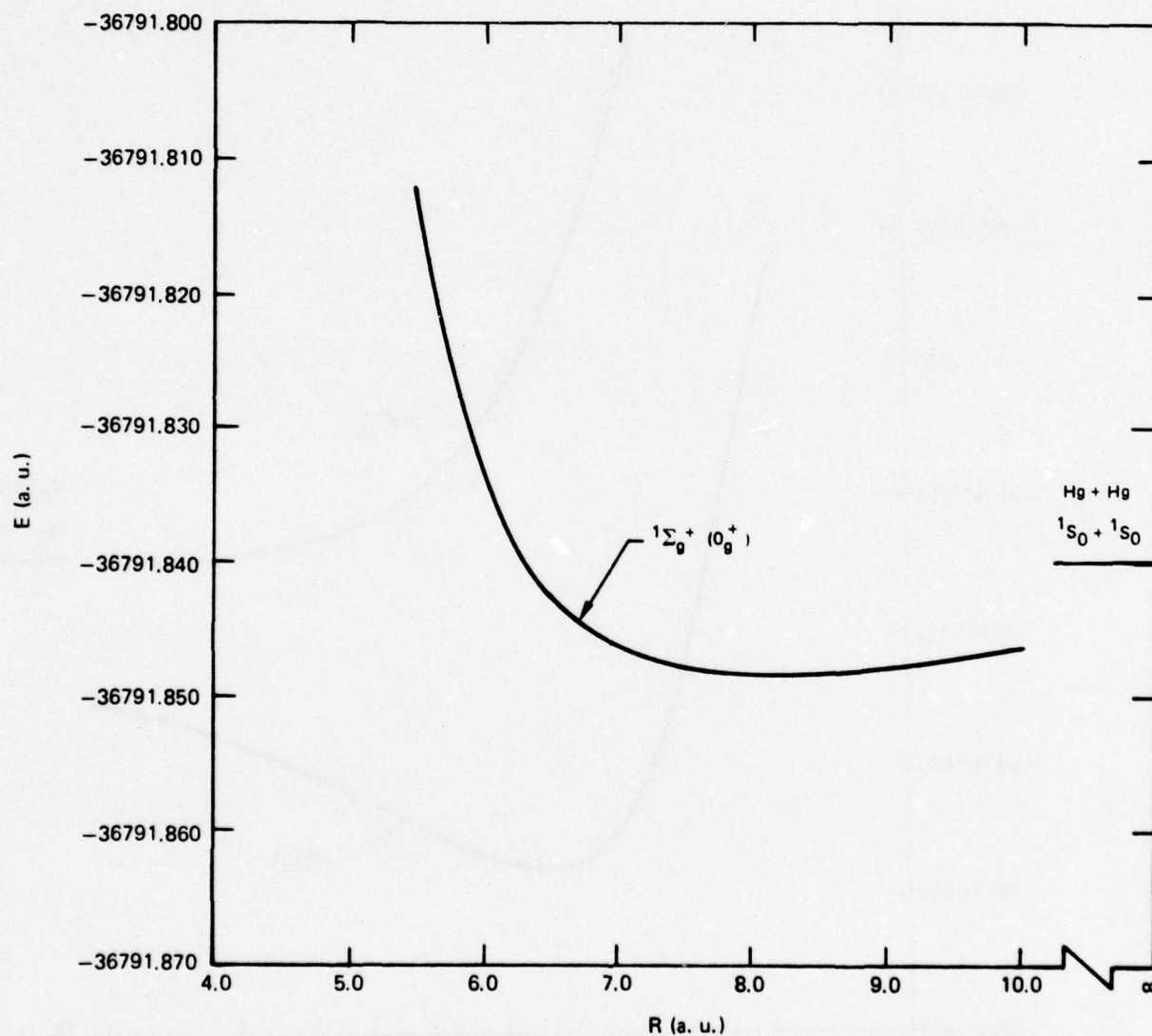
2. "Photodissociation of Noble Gas Dimer Ions." H. H. Michels. Presented at the 30th Annual Gaseous Electronics Conference, Palo Alto, California, October 18-21, 1977.
3. "Theoretical Studies of the Energetics of Electronic Transition Lasers." H. H. Michels. Presented at the AFOSR/AFGL Chemical Dynamics Contractors' Meeting, Air Force Geophysics Lab, Hanscom Air Force Base, Bedford, Massachusetts, October 26-27, 1977.
4. "Electronic Structure of Noble Gas Dimer Ions." Presented at the 1978 Sanibel Symposium on Atomic, Molecular and Solid State Theory, Sheraton Palm Coast Inn, Daytona, Florida, March 10-16, 1978.

LOW-LYING POTENTIAL ENERGY CURVES FOR SiF

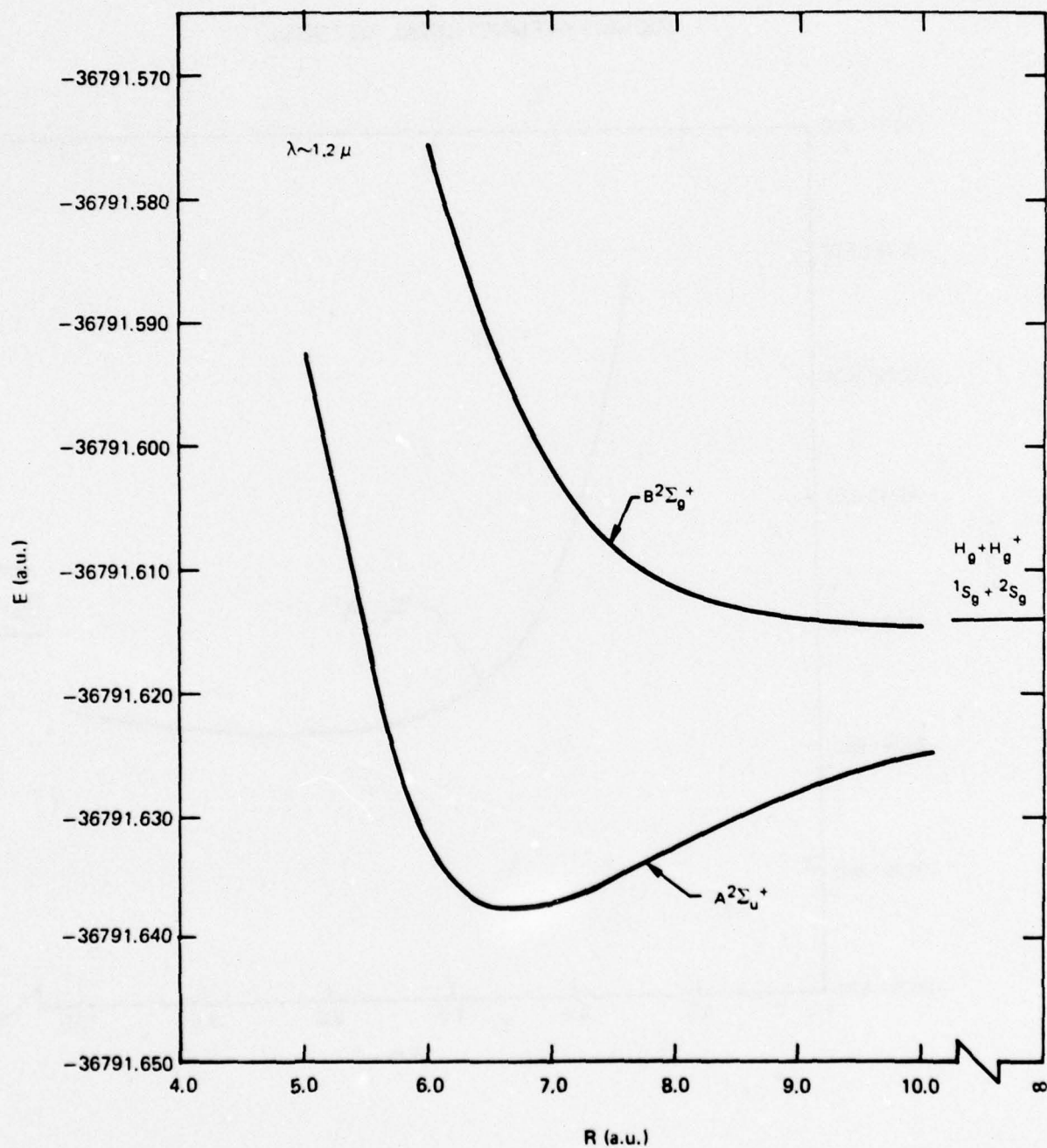


CORRELATION DIAGRAM FOR INTERMEDIATE COUPLING OF THE Hg₂ MOLECULEUNIQUE ASSIGNMENTS FROM (J₁, J₂) TO (A, S) COUPLING ARE INDICATED BY SOLID LINES

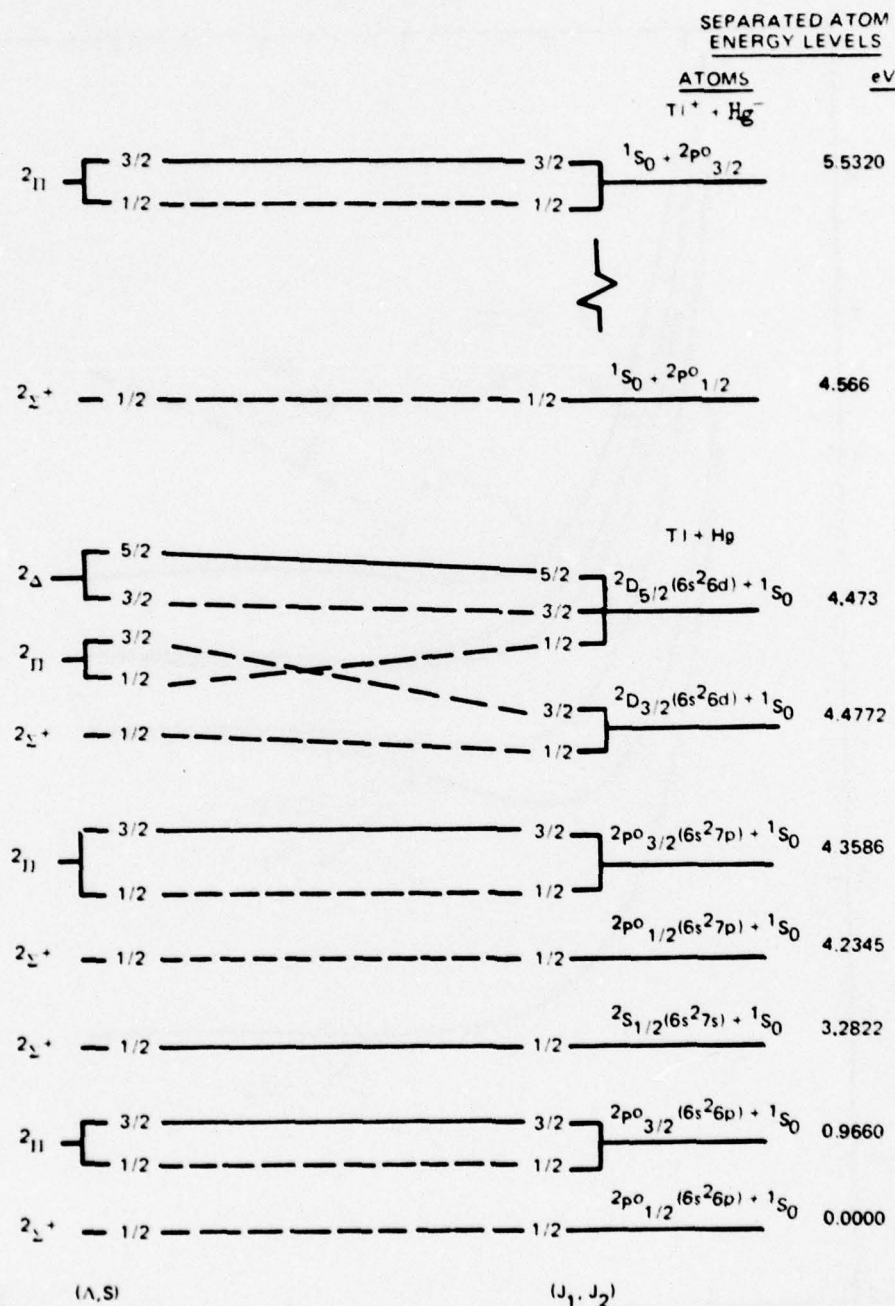
GROUND STATE POTENTIAL ENERGY CURVE FOR Hg_2
(DENSITY-FUNCTIONAL METHOD)



LOW-LYING POTENTIAL ENERGY CURVES FOR Hg_2^+
(DENSITY-FUNCTIONAL METHOD)



CORRELATION DIAGRAM FOR INTERMEDIATE COUPLING OF THE TI Hg MOLECULE



UNIQUE ASSIGNMENTS FROM (J_1, J_2) TO (Λ, S) COUPLING ARE INDICATED BY SOLID LINES

LOW-LYING POTENTIAL ENERGY CURVES FOR MgNa

(Ab Initio Method)

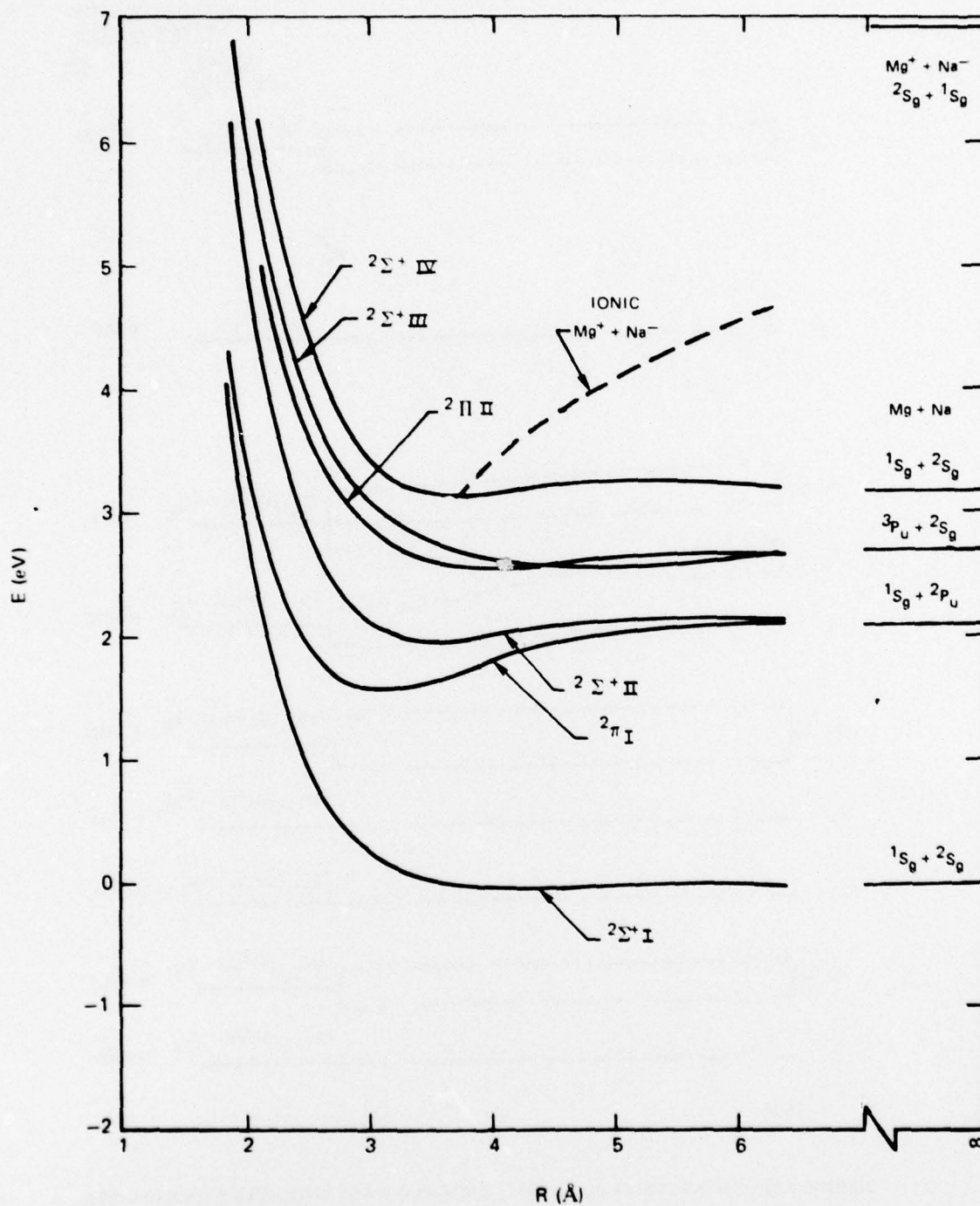


TABLE I

SiF/SiF₂ CORRELATIONS

<u>Dissociation Limit</u>	<u>eV</u>	<u>Molecular States</u>
SiF (X ² Π) + F (² P)	0.0	SiF ₂ (^{1,3} A ₁ , ^{1,3} B ₁)
SiF (A ² Σ ⁺) + F (² P)	2.83	SiF ₂ (^{1,3} A ₁ , ^{1,3} B ₁)
SiF (a ⁴ Σ ⁻) + F (² P)	3.70	SiF ₂ (^{3,5} A ₁ , ^{3,5} B ₁)
SiF ⁺ (X ¹ Σ ⁺) + F ⁻ (¹ S)	3.81	SiF ₂ (¹ A ₁)

TABLE II

LOW-LYING MOLECULAR STATES OF SiF AND THEIR DISSOCIATION LIMITS

<u>Dissociation Limit</u>	<u>eV</u>	<u>Molecular States</u>
Si + F		
$^3P_g (3s^2 3p^2) + ^2P_u (2p^5)$	0.0	$^2\Sigma^-(2), ^4\Sigma^-(2), ^2\Sigma^+(2), ^4\Sigma^+(1), ^2\Pi(2), ^4\Pi(2), ^2\Delta(1), ^4\Delta(1)$
$^1D_g (3s^2 3p^2) + ^2P_u (2p^5)$	0.781	$^2\Sigma^-(1), ^2\Sigma^+(2), ^2\Pi(2), ^2\Delta(2), ^2\Phi(1)$
$^1S_g (3s^2 3p^2) + ^2P_u (2p^5)$	1.908	$^2\Sigma^+(1), ^2\Pi(1)$
$^5S_u (3s 3p^3) + ^2P_u (2p^5)$	4.131	$^4\Sigma^-(1), ^6\Sigma^-(1), ^4\Pi(1), ^6\Pi(1)$
Si ⁺ + F ⁻		
$^2P_u (3s^2 3p) + ^1S_g (2p^6)$	4.701	$^2\Sigma^+(1), ^2\Pi(1)$

TABLE III
 LOW-LYING MOLECULAR STATES OF Hg_2^+
 AND THEIR DISSOCIATION LIMITS

<u>Dissociation Limits</u>	<u>eV</u>	<u>Molecular States</u>
$\text{Hg} + \text{Hg}^+$		
$1S_g(5d^{10}6s^2) + 2S_g(5d^{10}6s)$	0.0	$2\Sigma_g^+(1), 2\Sigma_u^+(1)$
$3P_u(5d^{10}6s6p) + 2S_g(5d^{10}6s)$	5.004	$2\Sigma_g^+(1), 2\Sigma_u^+(1), 4\Sigma_g^+(1),$ $4\Sigma_u^+(1), 2\Pi_g(1), 2\Pi_u(1),$ $4\Pi_g(1), 4\Pi_u(1)$
$1S_g(5d^{10}6s^2) + 2D_g(5d^96s^2)$	5.334	$2\Sigma_g^+(1), 2\Sigma_u^+(1),$ $2\Pi_g(1), 2\Pi_u(1),$ $2\Delta_g(1), 2\Delta_u(1)$
$1P_u(5d^{10}6s6p) + 2S_g(5d^{10}6s)$	6.702	$2\Sigma_g^+(1), 2\Sigma_u^+(1), 2\Pi_g(1),$ $2\Pi_u(1)$
$1S_g(5d^{10}6s^2) + 2P_u(5d^{10}6p)$	6.948	$2\Sigma_g^+(1), 2\Sigma_u^+(1),$ $2\Pi_g(1), 2\Pi_u(1)$

TABLE IV
 LOW-LYING MOLECULAR STATES OF MgNa
 AND THEIR DISSOCIATION LIMITS

<u>Dissociation Limits</u>	<u>eV</u>	<u>Molecular States</u>
Mg + Na		
$1S_g(3s^2) + 2S_g(3s)$	0.0	$2\Sigma^+(1)$
$1S_g(3s^2) + 2P_u(3p)$	2.103	$2\Sigma^+(1), 2\Pi(1)$
$3P_u(3s3p) + 2S_g(3s)$	2.712	$2\Sigma^+(1), 4\Sigma^+(1), 2\Pi(1), 4\Pi(1)$
$1S_g(3s^2) + 2S_g(4s)$	3.191	$2\Sigma^+(1)$
Mg ⁺ + Na ⁻		
$2S_g(3s) + 1S_g(3s^2)$	6.975	$2\Sigma^+(1)$

APPENDIX A

ELECTRONIC STRUCTURE OF THE NOBLE GAS DIMER IONS*

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ABSTRACT

A systematic study of the electronic structure and chemical binding in the dimer ion sequence, Ne_2^+ , Ar_2^+ , Kr_2^+ and Xe_2^+ , has been carried out using both density functional and ab initio configuration interaction computational approaches. This study includes detailed calculations of the pertinent potential energy curves and an analysis of the calculated spectroscopic properties of the bound $A \ ^2\Sigma_u^+ (1/2_u)$ state of these ions.

* Supported in part by the Air Force Office of Scientific Research under Contract F49620-77-C-0064

APPENDIX B

CONFIGURATION INTERACTION STUDIES OF THE HeH^+ MOLECULAR ION.
IV. THE TRIPLET SIGMA, PI AND DELTA STATES.*

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ABSTRACT

The method of superposition of configurations was applied to the triplet sigma, pi, and delta states of HeH^+ which correlate to the separated atom states of principle quantum number less than or equal to 3. The calculations were done for internuclear separations, $0 \leq R \leq 65.5$ a.u., on a mesh adequate for interpolation. Similar calculations on the singlet states have already been reported. The present calculations complete the accurate evaluation of the potential energy curves for this system which are required for low- and intermediate-energy collision studies. In addition to the energy eigenvalues and eigenfunctions, dipole, gradient and radial coupling matrix elements were calculated for the sigma and pi states. Primarily, this paper presents information on the eigenvalues. The accuracy of the triplet-state calculations is comparable to that obtained for the singlet states. The similarities and differences in the pattern of avoided crossings for the triplet and singlet states are exhibited. These are mainly determined by the differences in the triplet and singlet energy-level schemes of the united and separated atoms.

* Supported in part by the Air Force Office of Scientific Research under Contract F49620-77-C-0064.

APPENDIX C

ELECTRONIC STRUCTURE OF THE NOBLE GAS DIMER IONS.

I. POTENTIAL ENERGY CURVES AND SPECTROSCOPIC CONSTANTS*

H. H. Michels and R. H. Hobbs
United Technologies Research Center
East Hartford, Connecticut 06108

ABSTRACT

A systematic study of the electronic structure and chemical binding in the dimer ion sequence, Ne_2^+ , Ar_2^+ , Kr_2^+ and Xe_2^+ , has been carried out using both density functional and ab initio configuration-interaction computational techniques. This study includes detailed calculations of the pertinent potential energy curves and an analysis of the calculated spectroscopic properties of the bound states of these ions. A regular progression is found in the spectroscopic properties for the ground $A^2\Sigma^+_{1/2u}$ state which leads to some remarkably simple conclusions concerning the nature of the binding and the size of these dimer ions. For the heavier systems, Kr_2^+ and Xe_2^+ , spin-orbit coupling becomes important, resulting in a strong mixture of the Λ -s coupled Σ and Π states. This mixing affects the strength of the binding in the ground state. A comparison with other ab initio studies and an analysis of the asymptotic behavior at large internuclear separations is given.

These dimer ion species illustrate the classic Hartree-Fock symmetry dilemma arising from improper dissociation character. The nature of this problem for ionized homopolar species is discussed.

* Supported in part by the Air Force Office of Scientific Research under Contract F49620-77-C-0064.

APPENDIX D

ELECTRONIC STRUCTURE OF THE NOBLE GAS DIMER IONS.

II. ABSORPTION SPECTRUM FOR THE $A \ ^2\Sigma_g^+ \rightarrow D \ ^2\Sigma_g^+$ SYSTEM*

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ABSTRACT

A systematic study of the electronic structure and chemical binding in the dimer ion sequence, Ne_2^+ , Ar_2^+ , Kr_2^+ and Xe_2^+ , has been carried out using both density function and ab initio configuration interaction computational approaches. From the results of this study, the absorption spectrum for the UV transitions of the $A \ ^2\Sigma_u^+ \rightarrow D \ ^2\Sigma_g^+$ system has been calculated.

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APPENDIX E

ELECTRONIC STRUCTURE OF THE NOBLE GAS DIMER IONS.
III. ABSORPTION SPECTRUM FOR THE $A \ ^2\Sigma_u^+ \rightarrow B \ ^2\Pi_g$ SYSTEM*

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ABSTRACT

A systematic study of the electronic structure and chemical binding of the dimer ion sequence, Ne_2^+ , Ar_2^+ , Kr_2^+ and Xe_2^+ , has been carried out using both density functional and ab initio configuration interaction computational approaches. From the results of this study, the absorption spectrum for the visible/IR transition of the $A \ ^2\Sigma_u^+ \rightarrow B \ ^2\Pi_g$ system has been calculated.

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APPENDIX F

ELECTRONIC STRUCTURE OF EXCITED STATES
OF SELECTED ATMOSPHERIC SYSTEMS*

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I. INTRODUCTION

In order to evaluate the thermodynamic and radiation properties of a natural or perturbed state of the upper atmosphere or ionosphere, the thermal and transport properties of heated air are required. Such properties are also of particular interest in plasma physics, in gas laser systems, and in basic studies of airglow and the aurora. In the latter area, the release of certain chemical species into the upper atmosphere results in luminous clouds that display the resonance electronic-vibrational-rotation spectrum of the released species. Such spectra are seen in rocket releases of chemicals for upper atmospheric studies and upon reentry into the atmosphere of artificial satellites. Of particular interest in this connection is the observed spectra of certain metallic oxides and air diatomic species. From band intensity distribution of the spectra, and knowledge of the f -values for electronic and vibrational transitions, the local conditions of the atmosphere can be determined (Ref. 1).

Present theoretical efforts which are directed toward a more complete and realistic analysis of the transport equations governing atmospheric relaxation and the propagation of artificial disturbances require detailed information of thermal opacities and LWIR absorption in regions of temperature and pressure where molecular effects are important (Refs. 2, 3). Although various experimental techniques have been employed for both atomic and molecular systems, theoretical studies have been largely confined to an analysis of the properties (bound-bound, bound-free and free-free) of atomic systems (Refs. 4, 5). This has been due in large part to the unavailability of reliable wavefunctions for diatomic molecular systems, and particularly for excited states

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or states of open-shell structures. More recently (Refs. 6-9), reliable theoretical procedures have been prescribed for such systems which have resulted in the development of practical computational programs.

The theoretical analysis of atmospheric reactions requires the knowledge of the electronic structure of the ground and low-lying excited states of atoms, ions and small molecular clusters of nitrogen and oxygen and, in certain regions, the interaction of water or other small molecules with these clusters. Because of the computational complexity for systems with large numbers of electrons, traditional ab initio theoretical methods are difficult and expensive to apply. However, no clear alternative choice is currently on the horizon, although progress continues in semiempirical and perturbative approaches to the calculation of electronic structure. Such approaches have met with limited success in applications to electronically excited states of molecules. Ab initio computational programs based on the variational theorem, incorporating analytic basis functions and coupled with a configuration interaction analysis, remain the backbone of our techniques, for studies to chemical accuracy, which are applicable to systems such as the atmospheric diatomic molecules and ions.

The potential curves derived from such calculations can often be empirically improved by comparison with so-called experimental curves derived from observed spectroscopic data, using RKR or other inversion procedures. It is often found, particularly for the atmospheric systems, that the remaining correlation errors in a configuration interaction (CI) calculation are similar for many excited electronic states of the same symmetry or principle molecular orbital description. Thus, it is often possible to calibrate an entire family of calculated excited state potential curves to near-spectroscopic accuracy. Such a procedure has been applied to the systems described here.

The particular choice of the atmospheric systems to be presented here proved to be somewhat of a problem. Calculations for the N_2 molecule, including all low-lying valence and Rydberg states, had been performed several years ago (Ref. 10) as had a fairly extensive set of calculations for O_2^- (Ref. 11). Gilmore has described the known spectroscopic states for N_2 , O_2 , NO and several states of their corresponding positive and negative ions (Ref. 12). A complete analysis of all of the valence and low-lying Rydberg states for N_2 , O_2 and NO including ions, seemed too formidable (and expensive) a task, so the systems N_2 , O_2 , NO, O_2^- and NO^+ have been selected for inclusion in this review. This choice includes the most important atmospheric positive ion, NO^+ , and the chemically most interesting negative ion, O_2^- .

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The general composition of this article is as follows. We first present a critical review of the current status of electronic structure calculations for molecular systems. This is followed by a compilation of the potential energy curves, derived spectroscopic analysis and pertinent discussion of the atmospheric molecules selected above.

REFERENCES

1. Harang, O.: AlO Resonant Spectrum for Upper Atmosphere Temperature Determination. AFCRL-66-314, Environmental Research Paper No. 192, 1966.
2. Churchill, D. R. and R. E. Meyerott: J. Quant. Spectr. Radiative Transfer, 5, 69, 1965.
3. The Airglow and the Aurorae, edited by E. B. Armstrong and A. Dalgarno, Pergamon Press, New York, 1955.
4. Armstrong, B. H., R. R. Johnston and P. S. Kelly, Jr.: J. Quant. Spectr. Radiative Transfer, 5, 55, 1965.
5. Johnston, R. R., B. H. Armstrong and O. R. Platas: J. Quant. Spectr. Radiative Transfer, 5, 49, 1965.
6. Harris, F. E. and H. H. Michels: Int. J. Quantum Chem., 1S, 329, 1967.
7. Krauss, M.: Compendium of ab initio Calculations of Molecular Energies and Properties. NBS Technical Note 438, 1967.
8. Wahl, A. C., P. J. Bertoncini, G. Das and T. L. Gilbert: Int. J. Quantum Chem., 1S, 123, 1967.
9. Schaefer, H. F.: Electronic Structure of Atoms and Molecules. Addison-Wesley Publishing Co., 1972.
10. Michels, H. H.: J. Chem. Phys., 53, 841, 1970.
11. Michels, H. H.: Electronic and Atomic Collisions, Volume 2, edited by L. M. Branscomb, North Holland Publishing Co., Amsterdam, 1170, 1971.
12. Gilmore, F. R.: J. Quant. Spectr. Radiative Transfer, 5, 369, 1965.